Quantification of Variability and Uncertainty for Air Toxic Emission Inventories with Censored Emission Factor Data

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Probabilistic emission inventories were developed for urban air toxic emissions of benzene, formaldehyde, chromium, and arsenic for the example of Houston. Variability and uncertainty in emission factors were quantified for 71–97% of total emissions, depending upon the pollutant and data availability. Parametric distributions for interunit variability were fit using maximum likelihood estimation (MLE), and uncertainty in mean emission factors was estimated using parametric bootstrap simulation. For data sets containing one or more nondetected values, empirical bootstrap simulation was used to randomly sample detection limits for nondetected values and observations for sample values, and parametric distributions for variability were fit using MLE estimators for censored data. The goodness-of-fit for censored data was evaluated by comparison of cumulative distributions of bootstrap confidence intervals and empirical data. The emission inventory 95% uncertainty ranges are as small as −25% to +42% for chromium to as large as −75% to +224% for arsenic with correlated surrogates. Uncertainty was dominated by only a few source categories. Recommendations are made for future improvements to the analysis.

Introduction

The characterization and quantification of uncertainty and variability in air toxic inventories are important to prevent erroneous inferences in air quality modeling and exposure assessment, which may lead to major environmental policy implications. This paper presents a methodology to accomplish such quantification. This work has significant applications in air quality modeling and can provide much better understanding and quantification of exposure and risk assessment of hazardous air pollutants. The main contributions of this paper are to show how statistical techniques of maximum likelihood estimation (MLE) and bootstrap simulation can be combined to enable quantification of interunit variability and mean uncertainty in emission factors and to apply probabilistic methods to quantify, for the first time, the range of uncertainty in urban-scale hazardous air pollutant emission inventories via a case study.

The focus of the case study is on selected air toxic pollutants for the Houston, TX, urban area. The U.S. Environmental Protection Agency has developed a priority list of 33 urban air toxics for additional assessment of the health effects of air toxics in urban areas (*1*). Pollutants for which sufficient data were available to support a probabilistic analysis of air toxic emissions include chromium, formaldehyde, benzene, and arsenic, which have risk-related rankings of 5, 6, 10, and 17, respectively, on a nationwide basis, among the listed 33 urban air toxics. Houston was selected as the basis for a case study because it has been the subject of extensive study by others using deterministic methods (*2*).

Urban air toxic emissions are subject to both variability and uncertainty. Variability refers to the heterogeneity across different elements of a population over time or space (*3*, *4*). Variability in emissions arises because of differences in feedstocks, ambient conditions, design, or operational practices among facilities (*5*–*10*). Uncertainty is lack of knowledge about the true value of a quantity (*4*, *11*). Uncertainty in emissions is attributable to random sampling error, measurement error, and nonrepresentativeness (*5*–*10*). Variability and uncertainty can be quantified simultaneously using a two-dimensional probabilistic framework (*3*, *4*, *6*–*10*, *12*).

Emission inventories (EIs) are commonly obtained by the product of emission factors and activity factors. EIs are used by federal, state, and local governments and by private corporations for (a) characterization of temporal emission trends, (b) emission budgeting for regulatory and compliance purpose, and (c) prediction of ambient pollutant concentrations using air quality models. If random errors in the EIs are not quantified, erroneous inferences could be made regarding trends in emissions, source apportionment, compliance, and the relationship between emissions and ambient air quality (*13*).

The National Research Council (NRC) recommends that quantifiable uncertainties be addressed in estimating mobile source emission factors (*14*), and logically, this recommendation should be extended to other source categories. The NRC has also addressed the need for quantification of uncertainties in emission inventories used in risk assessment (*15*). Probabilistic techniques have been applied to estimate uncertainty in emission factors for mobile sources, major stationary sources, and area sources, particularly for criteria pollutants (e.g., NO_x) and ozone precursors (e.g., volatile organic compounds) (*5*–*10*, *13*, *16*–*18*). Recent work regarding air toxic emission estimates has focused on situations in which there was only one detection limit (*10*, *13*). However, many air toxic data sets have multiple measurements below several different detection limits, since the detection limit is a function of the sample volumes and analytical methods applied separately to each measurement.

Quantifiable uncertainties based upon statistical analysis of empirical data include random sampling error and random measurement error. Random measurement error is accounted for because the observed variability in the data includes both the true variability and the random component of measurement error, which in turn influences the range of the sampling distribution of the mean (*19*).

The objectives of this paper are to (i) demonstrate the application of a methodology for quantification of variability and uncertainty in situations involving multiple detection limits, (ii) quantify variability and uncertainty in urban air toxic emission factors for a specific case study, (iii) develop probabilistic EIs for selected pollutants, and (iv) identify key sources of uncertainty in the probabilistic EIs.

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Methodology

Air toxic emission factor data often include one or more measurements below a detection limit. Such data are referred to as censored (*20*). Conventional methods of dealing with nondetected measurements typically involve replacing nondetected values with 0, half of the detection limit, or the detection limit. Such methods lead to biases in estimates of the mean and variance for interunit variability in emissions (*21, 22*). In contrast, the use of MLE to fit parametric probability distributions to nondetected data is asymptotically unbiased (*21*−*23*). The likelihood functions used for candidate parametric distributions are given in the Supporting Information (*23, 24*). For censored data, the likelihood function is based upon the cumulative probability of the detection limit, rather than the probability density of an observed value, conditional on parameter estimates. A fitted parametric distribution is an inference regarding the true but unknown population distribution of interunit variability in the emission factor. The uncertainty in the mean or other statistics of the fitted distribution is estimated using bootstrap simulation. Bootstrap simulation is a numerical method for estimation of confidence intervals based upon simulation of random sampling error using Monte Carlo simulation (*25*). There are also other methods in uncertainty analysis, such as likelihood-based methods (*26, 27*). Bootstrap simulation is especially efficient for situations in which sample sizes are small and data are skewed, and does not require any restrictive assumptions regarding sampling distributions such as normality (*19*). Therefore, bootstrap simulation is a suitable technique to apply to urban air toxic emission factors. Furthermore, bootstrap simulation enables uncertainty analysis for any statistic of interest (e.g., the mean) as well as for the cumulative distribution function of the estimated population distribution of the data set.

To apply bootstrap simulation to censored data, it is necessary to characterize whether each observation is a detected measurement or is below a detection limit. Thus, a binary indicator symbol is used for each observation. For detected values, the binary indicator is set to 0. For nondetected values, the binary indicator is set to 1 and the corresponding numerical value in the data is the detection limit. Therefore, it is possible to quantify the existence of multiple nondetected values in the data, each of which may have a different detection limit. In bootstrap simulation, the data and indicator symbol pairs are sampled together randomly with replacement n times to generate one bootstrap sample, where n is the sample size of the original data set. The process is repeated B times. To each of the B empirical bootstrap pair samples, the selected type of parametric distribution is fit using MLE. The resulting B realizations of any statistic of interest, such as the mean, variance, or distribution percentiles, characterize the sampling distribution of the statistic associated with random sampling error. These distributions are interpreted as representing the uncertainty in the statistic associated with the variability in the data, finite sample size, and data censoring (*23*).

Log-Normal, γ, and Weibull Distributions. For environmental data sets, such as concentrations or emission factors, log-normal, γ, and Weibull distributions are often chosen to represent variability (*3, 6*−*8, 28*). The log-normal distribution is nonnegative, positively skewed, and based upon the central limit theorem applied to multiplicative processes; therefore, this distribution often well-describes data for physical quantities that arise from multiplicative processes, such as mixing or dilution (*29, 30*). The γ distribution is nonnegative, positively skewed, and similar to the log-normal distribution in many cases but is less "tail heavy" (*3*). The Weibull distribution is a flexible nonnegative distribution that can assume negatively skewed, symmetric, or positively skewed shapes and has been used to describe air pollutant con-

centrations (*3, 28*). These three distribution types are used as candidates for describing interunit variability in censored air toxic emission factor data.

Goodness-of-Fit Test. The goodness-of-fit of a parametric distribution fit to data was evaluated by comparing the bootstrap confidence intervals of the fitted cumulative distribution function (CDF) with an empirical distribution of the original sample data. Generally, the fit is taken as a reasonable one if 95% of the data will fall inside a 95% confidence interval of the CDF of a fitted distribution (*19*). The larger the proportion of data contained within the confidence intervals, the greater the preference for the particular candidate distribution model. The details of the procedure are illustrated in case studies. There are also alternative methods for the goodness-of-fit test, such as the Kaplan−Meier estimator. In previous work, the confidence interval calculated by the Kaplan−Meier estimator has been compared with bootstrap confidence intervals. Both produce similar results. We choose the latter because it is more informative with regard to many statistics and probability ranges for the intervals (*23*).

Monte Carlo Simulation of Uncertainty in the Emission Inventory Model. The emission inventory for a pollutant is given by

$$EI = \sum (EF_i)(AF_i) \qquad (1)$$

where EF_i = emission factor for source i (mass emissions per unit of activity) and AF_i = activity factor for source i (unit of activity). On the basis of selection of the preferred probability distribution model to represent interunit variability in the emission factor, uncertainty was estimated for the mean emission factor using bootstrap simulation. Uncertainty in the activity factor was estimated on the basis of judgment. The uncertainty in the emission inventory was simulated using Monte Carlo simulation (*3, 11*). A total of 500 random numbers were first generated from the distributions of the mean emission factors and activity factors. They were input into eq 1. Thus, 500 random values of the outputs were obtained, resulting in an estimate of the probability distribution of uncertainty in the total inventory.

Identification of Key Sources of Uncertainty. The sensitivity of uncertainty in the total emission inventory for a pollutant to uncertainty in the individual inputs to the inventory was assessed using Spearman correlation coefficients, which measure the strength of the monotonic relationship between two random variables (*3*). Inputs that had a statistically significant correlation with the outputs were identified as sensitive inputs. The larger the magnitude of the correlation, the greater the sensitivity. Identification of the most highly sensitive inputs enables targeting of resources in future work to collect more or better information to reduce uncertainty.

Houston Emission Inventory

A probabilistic emission inventory for benzene, formaldehyde, chromium, and arsenic was developed for Houston on the basis of the deterministic 1996 inventory. The 1996 inventory was selected because it has been used for a variety of analyses and was the most recent readily available. The focus of the uncertainty analysis was on major source categories. For example, for benzene, the sources emitting more than 20 t/yr were defined as major source categories. There are 24 major source categories, and these account for 90% of the total estimated emissions. For formaldehyde, there are 12 major source categories accounting for 99% of the total estimated emissions. For chromium and arsenic, there are 27 and 20 major source categories accounting for 71% and 81% of the total emissions, respectively. The point estimates of the emissions for each major source category
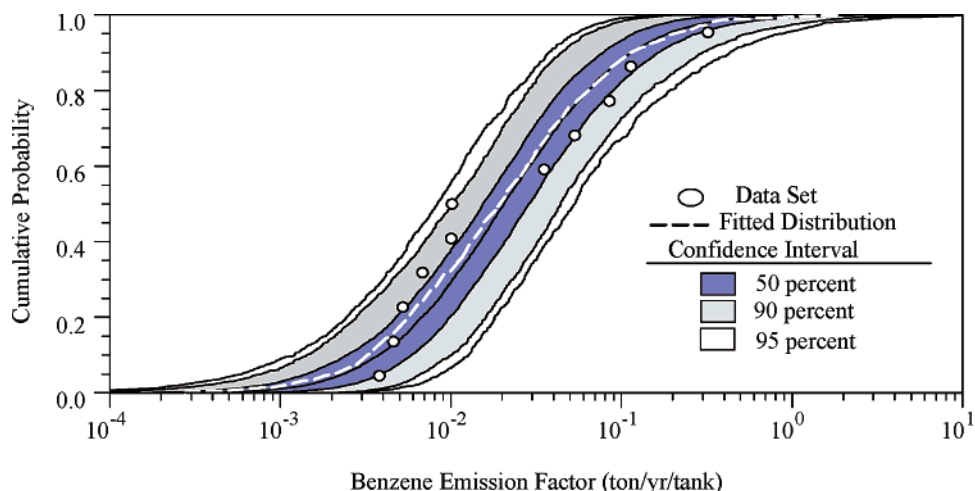
FIGURE 1. Variability and uncertainty in the benzene emission factor for case 3b (nonwinter storage losses at a typical gasoline bulk terminal) estimated on the basis of a log-normal distribution.

are in Tables S-1—S-4 for benzene, formaldehyde, chromium, and arsenic in the Supporting Information, respectively.

Data for the interunit variability in emission factors were identified for each pollutant and source category, where available, on the basis of information reported by the EPA and others, such as the California Air Resources Board and the Coordinating Research Council (*5, 7, 8, 31—41*). A detailed summary of the sources of data for each source category are given in the Supporting Information in Tables S-5—S-8 for benzene, formaldehyde, chromium, and arsenic, respectively. For many source categories, directly relevant data were available via which to estimate interunit variability and to infer uncertainty in the mean emission factor. For other source categories, directly relevant data were not available. Therefore, judgments were made regarding surrogates for which uncertainty estimates were likely to be similar. For example, directly relevant sample data were available for intervehicle variability in benzene emissions from light-duty gasoline vehicles. However, such data were not available for heavy-duty gasoline vehicles. In this case, the relative range of uncertainty in mean benzene emissions for light-duty gasoline vehicles was used as a surrogate to estimate the relative range of uncertainty in mean benzene emissions for heavy-duty vehicles. A detailed discussion of the judgments made regarding surrogates is given in the Supporting Information.

The emissions for some source categories are estimated as the aggregation of several subcategories. As an example, uncertainty in benzene emissions for petroleum refineries was estimated on the basis of weights assigned to uncertainties in emissions for gasoline loading racks at bulk terminals and bulk plants, storage losses at a typical gasoline bulk terminal, wastewater treatment, emissions from a typical bulk plant, storage losses at a typical pipeline breakout station, emissions for a typical service station for petroleum refineries, and storage tanks for petroleum refineries. For each of the subcategories, data were available from which to quantify relative uncertainty in mean emission rates.

For mobile sources, uncertainty in emissions was estimated on the basis of the product of uncertainty in the emission rate of total hydrocarbons and of the uncertainty in the percentage of total hydrocarbons emitted as a specific air toxic. Details are shown in the Supporting Information.

Directly relevant uncertainty data were available for as little as 45% of the major source emissions for formaldehyde to as much as 74% in the case of arsenic. When both direct and surrogate uncertainty data are considered, uncertainty is estimated for as little as 71% of the nominal emission inventory in the case of chromium to 90% or more of the

inventories in the cases of benzene and formaldehyde. Thus, for all four pollutants, it was possible to quantify uncertainty for the majority of the emission inventories.

Results

The variability and uncertainty in the urban air toxic emission factors for different source categories of the Houston area were quantified. Probabilistic emission inventories were developed considering the uncertainty in the emission and activity factors. The key sources of uncertainty were identified by sensitivity analysis.

Quantification of Variability and Uncertainty in Emission Factors. Log-normal, γ, and Weibull distributions were fit to the available emission factor data for interunit variability. In terms of the goodness-of-fit test, the adequacy and preference of the fit were evaluated graphically on the basis of comparison of bootstrap confidence intervals of the fitted CDF to the empirical distribution of the data for both uncensored and censored data. For each case, one or more distribution types are judged to be adequate. The preferred distributions for interunit variability are given in Tables S-1—S-4 for benzene, formaldehyde, chromium, and arsenic, respectively, including the parameter estimates. The interunit variability in the urban air toxic emission factors is typically large. For example, 13 out of 16 empirical benzene emission factor data sets have a 95% probability ratio larger than 2 orders of magnitude based upon the preferred distribution type as given in the Supporting Information. The 95% probability ratio is defined as the ratio of the upper level to the lower level of the 95% probability range for interunit variability.

Uncertainty in the mean was estimated using parametric bootstrap simulation for the cases with no censoring and with the empirical bootstrap pair approach previously described for cases with censoring. The resulting estimates of the 95% confidence intervals for the means are summarized in Tables S-1—S-4.

To illustrate the details of the approach via which variability and uncertainty in an emission factor were quantified, an example case study is given for the benzene emission factors for case 3b, nonwinter storage losses at a typical gasoline bulk terminal. The emission factor data contain 11 detected values. Bootstrap simulation was used to estimate the confidence intervals of the fitted CDF. Figures 1 and S-2 show an empirical distribution of the data, the CDF for the distribution fitted to the original data, and the bootstrap confidence bands for the cases based on log-normal and Weibull distributions, respectively, which are visually
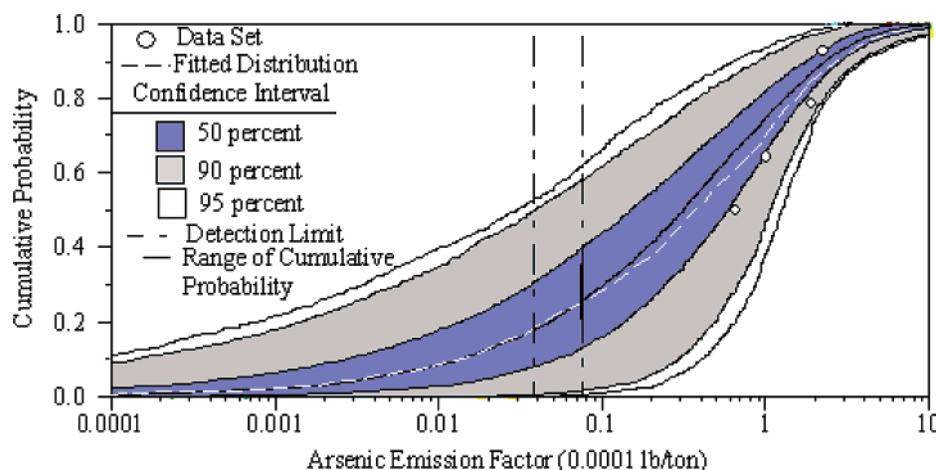
FIGURE 2. Variability and uncertainty in the arsenic emission factor for case 14 (external combustion boilers—industrial wood) estimated on the basis of a Weibull distribution.

judged to be better ones to represent the data. The data points are plotted using the Hazen plotting position (*3*). For log-normal and Weibull distributions, the 95% confidence intervals of the CDF enclose all of the data points. Therefore, both the log-normal and Weibull distributions are adequate fits to these data. However, the Weibull distribution has a heavy lower tail that appears to give inappropriate weight to small values not consistent with the data set. Thus, the log-normal distribution was selected as a preferred fit. Therefore, the recommended 95% confidence interval relative to the mean value is −72% to +185% based on log-normal distribution for this case.

The selection of a preferred distribution for a censored case with multiple detection limits is illustrated by the arsenic emission factors for case 14, external combustion boilers— industrial wood. The emission factor data contain five detected and two censored values. Log-normal and Weibull distributions are taken as candidate parametric distributions as they graphically describe the data better. Figures 2 and S-7 show the variability and uncertainty based upon Weibull and log-normal distributions, respectively. Because each censored value has a different detection limit, two detection limits are indicated. For the detected points, four of them are larger and one is smaller than the larger detection limit. The former four points have exact ranks and exact empirical cumulative probabilities. For the smallest detected data point, there is ambiguity in the ranks and cumulative probability. These data points could have a rank as low as 2 or as large as 3, depending upon the true but unknown value for the nondetected measurement corresponding to the larger detection limit. This ambiguity is depicted by a vertical solid line, instead of a point. The Weibull distribution was judged to better describe the arsenic emission factor data since the detected data points are closer to the 50% confidence interval in Figure 2 than for log-normal distribution in Figure S-7.

Development of Probabilistic Emission Inventories. Probabilistic emission inventories were developed on the basis of probabilistic mean emission factors and activity factors. Data regarding uncertainty in the activity were not available. It is expected that there is uncertainty in the activity factors. However, in the absence of empirical data, a judgment was made to assign a nominal range of uncertainties to the activity factors. For each source category, a 95% confidence interval in the mean of the activity factor was assumed ranging from −10% to +10%. Therefore, the normalized uncertainty estimates of the activity factors were generated from independent normal distributions with a mean of 1.0 and standard deviation of 0.05. In principle, uncertainty in activity factors

should be quantifiable on the basis of statistical error associated with surveying techniques used to obtain activity information or on the basis of elicitation of expert judgment of those who prepare activity factor estimates. In some cases, such as for energy statistics, error estimates of activity statistics are routinely assessed and are often very small (*42*), but in many other fields such assessments are not available. However, it was beyond the scope of this work to address this issue in detail. Instead, the approach taken here was to create a nominal placeholder estimate of uncertainty for activity factors that demonstrates a methodology for incorporating activity factor uncertainty into a probabilistic inventory. The uncertainty estimate used for the activity factor is sufficiently small that the analysis results are essentially influenced only by the emission factor uncertainties. The total uncertainty for each source category was calculated by multiplying the recommended uncertainty estimates of the emission factor by the uncertainty estimates of the corresponding activity factor. The uncertainty estimates were represented by uncertainty factors, which are random numbers generated from the distribution of mean emission factors and activity factors by Monte Carlo simulation. On the basis of the uncertainty of each source category, a probabilistic emission inventory was developed:

$$PEI = \sum_{i=1}^{n} [(UF_{EF,i})(UF_{AF,i})(EI_i)] \qquad (2)$$

where $UF_{EF,i}$ = normalized uncertainty factor of emission factors for source i, $UF_{AF,i}$ = normalized uncertainty factor of activity factors for source i, and EI_i = emission inventory from source i (t/yr).

For the emission inventory from each source, the uncertainty was quantified on the basis of eq 2. Table 1 summarizes the results of the mean, estimated median, and 95% confidence intervals in the emissions for the top five sources for benzene, formaldehyde, chromium, and arsenic.

In estimating the probabilistic total emission inventory, two cases were considered to gain insight regarding whether the use of surrogate uncertainty estimates has a significant effect on the results for uncertainty in the total inventory. In the first case, because the same source of information was used for two or more categories, 100% correlation of the uncertainty in the surrogate source and the target source was assumed. For example, for benzene the uncertainty in the emission factor for light-duty gasoline trucks was correlated with that for light-duty gasoline vehicles. In the

TABLE 1. Results of the Mean, Estimated Median, and 95% Confidence Interval in the Emission for the Top Five and All Sources for Benzene, Formaldehyde, Chromium, and Arsenic

pollutant	source	emissions (t/yr)		
		mean	median	95% CI[a]
benzene	mobile source, light-duty gasoline vehicles	1164	829	139−4040
	mobile source, light-duty gasoline trucks	846	603	102−2940
	petroleum refinery	714	572	324−1837
	four-stroke lawn and garden engines	687	667	465−1029
	two-stroke lawn and garden engines	234	231	158−324
	total for all sources	4600	4047	2500−9700
formaldehyde	nonroad mobile source	1282	1261	912−1720
	on-road mobile source	977	775	237−2700
	internal combustion engines	144	90	34−401
	oil and gas extraction	99.5	99	87−112
	chemical and allied processes	69.7	70	61−79
	total for all sources	2700	2531	1700−4600
chromium	petroleum refineries, catalytic cracking	1.87	1.86	1.67−2.04
	external coal combustion utility boilers	1.12	1.00	0.45−2.58
	marine vessels, commercial	1.03	na[b]	na[b]
	chemical manufacturing−fuel-fired equipment−process heaters	0.81	0.63	0.17−2.43
	all off-highway vehicles, diesel	0.34	na[b]	na[b]
	total for all sources	5	4.8	3.7−7
arsenic	external coal combustion utility boilers	1.77	0.80	0.15−6.56
	hazardous waste incineration	0.35	0.34	0.23−0.52
	Portland cement manufacturing	0.24	na[b]	na[b]
	petroleum refineries, catalytic cracking	0.21	na[b]	na[b]
	marine vessels, commercial	0.20	na[b]	na[b]
	total for all sources	2.2	1.3	0.6−7.1

[a] 95% confidence interval. [b] Results are not available due to a lack of directly relevant or surrogate data.

TABLE 2. Results of the Uncertainties in the Total Emission Inventories for Benzene, Formaldehyde, Chromium, and Arsenic

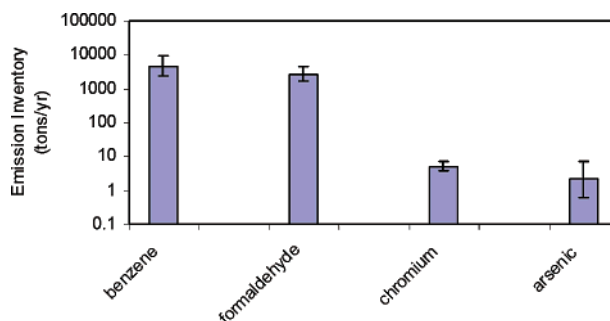| pollutant	95% confidence interval in the emission inventories (%), relative to the mean estimate	
	correlated surrogates	uncorrelated surrogates
benzene	−46 to +108	−41 to +77
formaldehyde	−36 to +69	−36 to +69
chromium	−25 to +42	−24 to +40
arsenic	−75 to +224	−74 to +222

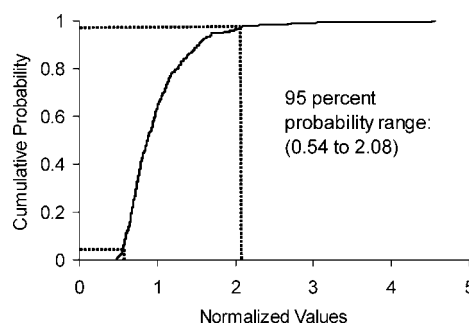FIGURE 3. Total emissions and 95% confidence intervals for benzene, formaldehyde, chromium, and arsenic.

FIGURE 4. Weighted average uncertainty factor for benzene emissions for all source categories with correlated surrogates.

second case, statistical independence was assumed since in the real world emission for one source category might not be dependent on those in a different source category. The relative 95% confidence intervals of the mean are given in Table 2 for both cases. The absolute 95% uncertainty range for the total inventory for benzene is 2500−9700 t/yr versus 2700−8200 t/yr when the correlated and uncorrelated surrogates, respectively, were compared. For formaldehyde, chromium, and arsenic, there was no difference in the ranges between the two cases. For formaldehyde, the range of uncertainty in either case was from 1700 to 4600 t/yr. For chromium, the range was 3.7−7.0 t/yr, and for arsenic the range was 0.6−7.1 t/yr. Thus, there was not a substantial difference when correlated versus uncorrelated surrogates were compared, which indicates that the source categories for which surrogate data were used are not the most important contributors to overall uncertainty. The absolute values for the mean, median, and 95% confidence interval for the total emissions of the four air toxics are also given in Table 1 when correlated surrogates were used. Figure 3 shows bar graphs summarizing the total emissions and the estimated 95% confidence intervals for benzene, formaldehyde, chromium, and arsenic based on a log scale. It is apparent that arsenic emission has the largest relative uncertainty. Figure 4 shows the cumulative probability in the normalized mean

emission for benzene from all source categories with correlated surrogates. Figures for other cases are given in the Supporting Information.

For supporting details, please see Tables S-1−S-4 for benzene, formaldehyde, chromium, and arsenic, respectively, in the Supporting Information.

Sensitivity Analysis To Identify the Key Sources of Uncertainty. The rank correlation between the uncertainties in total emissions and the uncertainty in the emission factors of each source category was calculated considering both

correlated and uncorrelated surrogates. The results are given in Tables S-1–S-4 for the four pollutants.

For benzene, gasoline on-road mobile sources are the dominate source of uncertainty in the inventory. For formaldehyde, the on-road and nonroad mobile sources are the key sources of uncertainty. For chromium, the key sources of uncertainty are chemical manufacturing–fuel-fired equipment–process heaters, external coal combustion utility boilers, and hard chromium electroplating. For arsenic, external coal combustion utility boilers are the dominate source of uncertainty in the inventory. The other statistically significant correlations are smaller than 0.2 for each of the pollutants, indicating only weak sensitivity.

For chromium, there are no sample data for the third largest source category of marine commercial vessels. The point estimate for this category is comparable to that of source no. 2 that was identified as key source category. Therefore, if the uncertainty in the emission factors from source no. 3 is similar to or greater than that of source no. 2, it would also be a key source of uncertainty. Future evaluation for this source category is needed when new data are available.

For arsenic, there are no data for the third to the sixth largest source categories. In this case, the largest source category contributes most of the uncertainty as shown by the rank correlation of 0.99, and the second source category has a weak correlation of less than 0.2. Thus, it is likely that the third to the sixth largest source categories, which are small relative to the first, are not key sources of uncertainty.

Discussion

In the procedure to develop probabilistic emission inventory, directly relevant data were not available and judgments were made regarding surrogate relative uncertainty estimates for many source categories. For some source categories, it was necessary to weight data from subcategories; however, the results for uncertainty in the total inventory were not sensitive to judgments regarding these weights. In particular, either the ranges of uncertainty were similar among many of the subcategories or the source category was not important with regard to overall uncertainty in the inventory.

The key characteristics of the probabilistic analysis include (1) large ranges of interunit variability in emission factors for specific source categories, (2) mean emission factor uncertainty ranging from as small as approximately ±10% to as large as −99% to +600%, (3) relative uncertainty ranges in total emissions ranging from as small as approximately −25% to +42%, as in the case of chromium, to as large as −75% to +224%, in the case of arsenic, and (4) identification of a small number of key sources of uncertainty for each pollutant. Better data collection and reporting should be prioritized for the key source categories.

The quantified ranges of uncertainties for benzene, formaldehyde, chromium, and arsenic emissions in the Houston area take into account random sampling error and measurement error in emission factors. However, since information regarding the contribution of measurement error to each measurement is not available, the uncertainties caused by the two types of error are not separately quantified.

The averaging times of the emission measurements vary among the source categories and in many cases are not documented in the references from which the data were obtained. It is likely that most of the measurements are for relatively short averaging times on the order of minutes (e.g., for some mobile sources) to perhaps days (e.g., stack testing). Although the desired averaging time for exposure assessment purposes is one year or longer, the uncertainty in the mean emission estimates is influenced by the limited averaging time of the available data.

The probabilistic emission inventory developed here could be improved in several ways pending availability of additional data or the incorporation of a more extensive expert elicitation component. For example, although biases in the mean emission factors are suspected, especially for fugitive emissions and as a result of process upset, insufficient data were available via which to quantify such biases. Other possible sources of bias include lack of representative data (e.g., measurements may have been for load or operating conditions not typical of annual average in-use activity) and the use of surrogate data for source categories in which data were lacking or not readily available. Expert elicitation could be used to encode judgments regarding the additional uncertainty associated with nonrepresentative or surrogate data. As new data become available, the assessment can be updated. A key obstacle to quantification of uncertainty based upon statistical data analysis is obtaining the necessary data. Often, data are measured and reported by multiple organizations. In the long term, the development of a protocol for archiving such data and making the data available would facilitate probabilistic analysis.

The uncertainty in the activity factors here is based on an approximate judgment, mostly as an acknowledgment that uncertainty exists and as a placeholder pending better information. In the long term, the quantifiable uncertainty in the activity factors should be incorporated on the basis of expert judgment.

The results of this work demonstrate that random sampling error and measurement error in emission factors are substantial sources of quantifiable uncertainty in the emission inventories of benzene and formaldehyde in the Houston area. The positively skewed ranges of uncertainty appropriately account for the fact that emissions must be nonnegative. The MLE/bootstrap methodology used here provides asymptotically unbiased estimates of the mean, including for cases that involve nondetected data. The substantial ranges of uncertainty estimated here should be taken into account when air quality modeling and exposure assessment are conducted. Furthermore, the identification of key sources of uncertainty in the inventory serves as an aid to prioritizing resources for additional data collection or research to reduce uncertainty.

Acknowledgments

Supporting Information Available

Text, tables, and figures pertaining to details of the comparison of different methods to estimate uncertainty, the MLE parameter estimation method for censored data, variability and uncertainty results for the emission factors and emission inventories, specific sources of data for each emission factor, the methods used for quantification of uncertainty in mobile source emission factors and for source categories based upon aggregation of subcategories, and a graphical summary of the relative range of uncertainty in total emissions for each pollutant for both correlated and uncorrelated surrogates. This material is available free of charge via the Internet at http//:pubs.acs.org.

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